MRC 2509

Second Quarterly Progress Report

HIGH TEMPERATURE THERMOELECTRIC GENERATOR

Contract Nr. AF 33(657)-7387
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NOTICE

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Submitted
to
Aeronautical Systems Division
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ABSTRACT

This report covers the work done from 1 January through 30 March 1962 under Contract No. AF 33(657)-7387 on the development of a 5-watt laboratory thermoelectric generator capable of operating at a hot junction temperature of 1200°C in a vacuum of 10^{-5} mm Hg. Fourteen candidate junction materials were screened for use with MCC 50 in the production of thermocouple modules. Of these, carbon, molybdenum and tungsten are being considered for the end product generator. Three methods for fabricating thermocouple modules with MCC 50 were studied and a hot-press/braze method selected for use in the making of modules for the end product.

In sublimation rate loss tests conducted for 500 hours at 1200°C at 10^{-5} to 10^{-6} mm Hg, MCC 50 thermoelectric material lost only 0.53% weight. The rate of sublimation loss appears to decrease with time. Measurements of electrical properties of modules, before and after 100 hour tests at 1200°C, indicate the end product generator can be operated well beyond 1000 hours, the design goal. Merit factors (Z) of MCC 50, based on extrapolations of thermal conductivity measurements from 1000°C, range from 0.6×10^{-3} to 1.1×10^{-3} °C^{-1} between 1200°C and 1500°C.

A 4-module prototype generator unit was constructed and is being tested at 1200°C in a vacuum to evaluate tentative design features of the end product generator.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Cont'd

LIST OF TABLES

LIST OF TABLES, Cont'd

I. INTRODUCTION

This report presents the results of work performed on Contract AF 33(657)-7387 during the period 1 January through 30 March 1962.

The objective is to conduct applied research and development on a laboratory-type high-temperature thermoelectric generator for use as an aerospace flight-vehicle power supply. More specifically, the project concerns design and fabrication of a nominal 5-watt power generator based on a new proprietary thermoelectric material, MCC 50, of Monsanto Chemical Company. Design goals and tests to be made are as follows:

1. The generator is to be a laboratory model, not one specifically designed for aerospace conditions. However, space conditions must be considered in the selection of design concept and components.

2. Generator hot junction shall be 1200-1500^{o}C with the cold junction between 500-700^{o}C.

3. The power output shall be a nominal 5 watts.

4. Sublimation tests on the thermoelectric materials are to be conducted in a vacuum of 10^{-5} mm Hg for at least 500 hr.

5. A lifetime of at least 1000 hr. is the design goal. However, the generator need be subjected to duration tests of 100 hr. or more of continuous operation in a vacuum of 10^{-5} mm Hg.

6. Electrical power characteristics of the generator are to be determined at various temperatures.

7. Thermal cycling tests on the thermoelectric material and representative generator sub-assemblies (modules) will be made. Pending successful completion of a 100-hr. duration test, the generator must be subjected to cycling tests to determine the effect of thermal contraction and expansions on performance.

To expedite development of the end product generator, thermocouple modules from each candidate junction material have been fabricated and tested. The module concept involves making and testing small thermoelectric generator module units similar to that shown in Figure 1. Such modules are more economically and readily fabricated than complete generators, and provide information on the mechanical strength, sublimation loss, electrical properties, thermal shock and solid-state diffusion characteristics of candidate junctions. In Addition to facilitating evaluation of a number of materials, the modular approach also permits the simultaneous investigation of techniques for joining junction materials to the thermoelectric material.

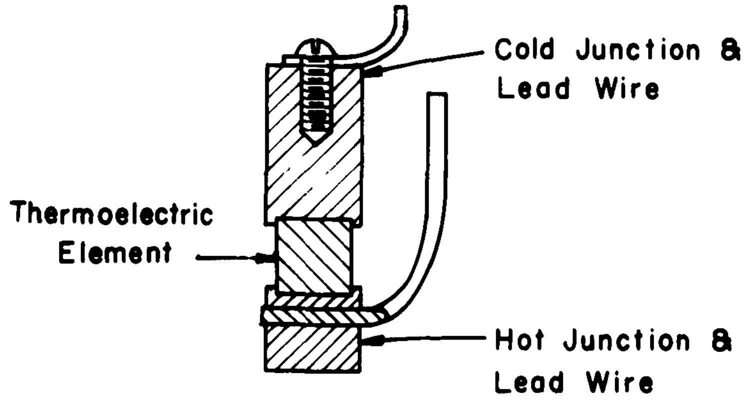

Figure 1. Simple Thermocouple Module for Use in Screening Junction Materials

After the number of candidate junction materials had been narrowed by screening tests, a 4-module prototype generator unit was fabricated and operated under high temperature and vacuum conditions to develop design information for the end product generator. This approach maximizes chances for success while minimizing the expense and risk of using unsuitable modules in the generator.

II. PROJECT RESULTS

The thermoelectric material upon which design of the 5-watt generator is based is a new proprietary research product, MCC 50, developed by Monsanto Chemical Company. The Seebeck coefficient (S) and the electrical resistivity (ρ) properties of MCC 50 have been established (See Figures 2 and 3) to temperatures in excess of 1200°C.[1]

The thermal conductivity (K) of MCC 50 ranges between 0.02 watt/cm°C and 0.04 watt/cm°C above 950°C. As shown in Figure 4, merit factors (Z) for MCC 50 range from less than 0.1×10^{-3} °C^{-1} at 300°C to extrapolated values ranging from 0.68×10^{-3} to 1.1×10^{-3} °C^{-1} at 1500°C corresponding to the difference in K reported by MRC and interpolated from NRL measurements.[2] A major task of this project is to develop thermal and electrical contacts of sufficiently low resistance to minimize junction energy losses in the end product generator.

To meet the design, fabrication and testing goals of the project, a three-phase program as outlined below is being followed:

PHASE I. Selection of junction materials and development of a method for joining them in modular form to the thermoelectric material.

PHASE II. Testing junction materials and modules for mechanical strength, sublimation losses, electrical properties, solid-state diffusion and resistance to thermal cycling.

PHASE III. Fabrication and testing of a 5-watt generator.

Results of activities carried on under each phase of the project program follow.

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(1) Values of S and ρ reported in Figures 2 and 3 were confirmed to about 950°C by the US Naval Engineering Experiment Station, 22 January 1962, Ref: NP/10310 (912) Report 9101586.

(2) Extrapolated from measurements of K for MCC 50 thermoelectric materials made at NRL using Skinner-type comparator apparatus.

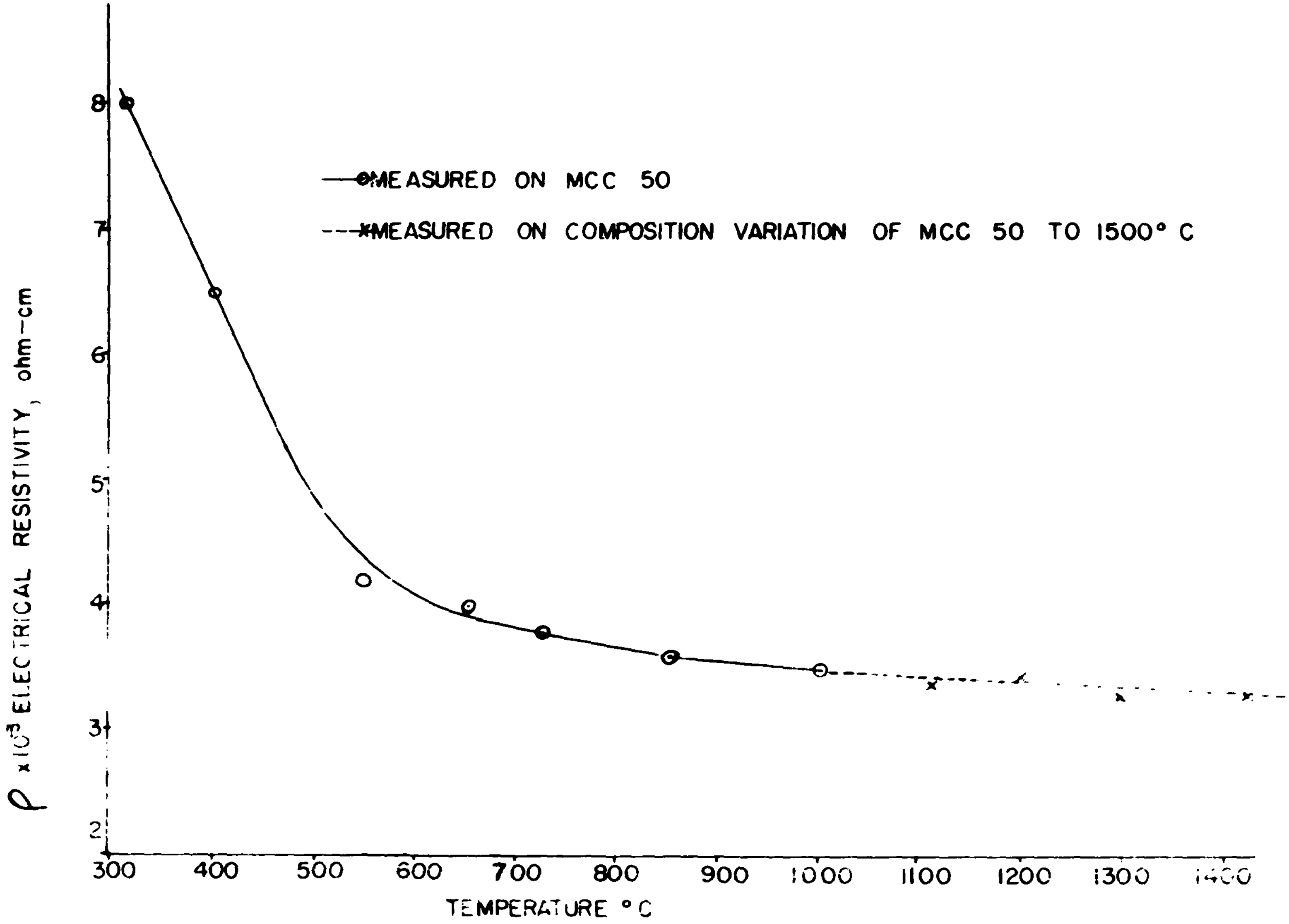

Figure 2. Electrical Resistivity vs. Temperature for MCC 50 Thermoelectric Material (Revised April 1962)

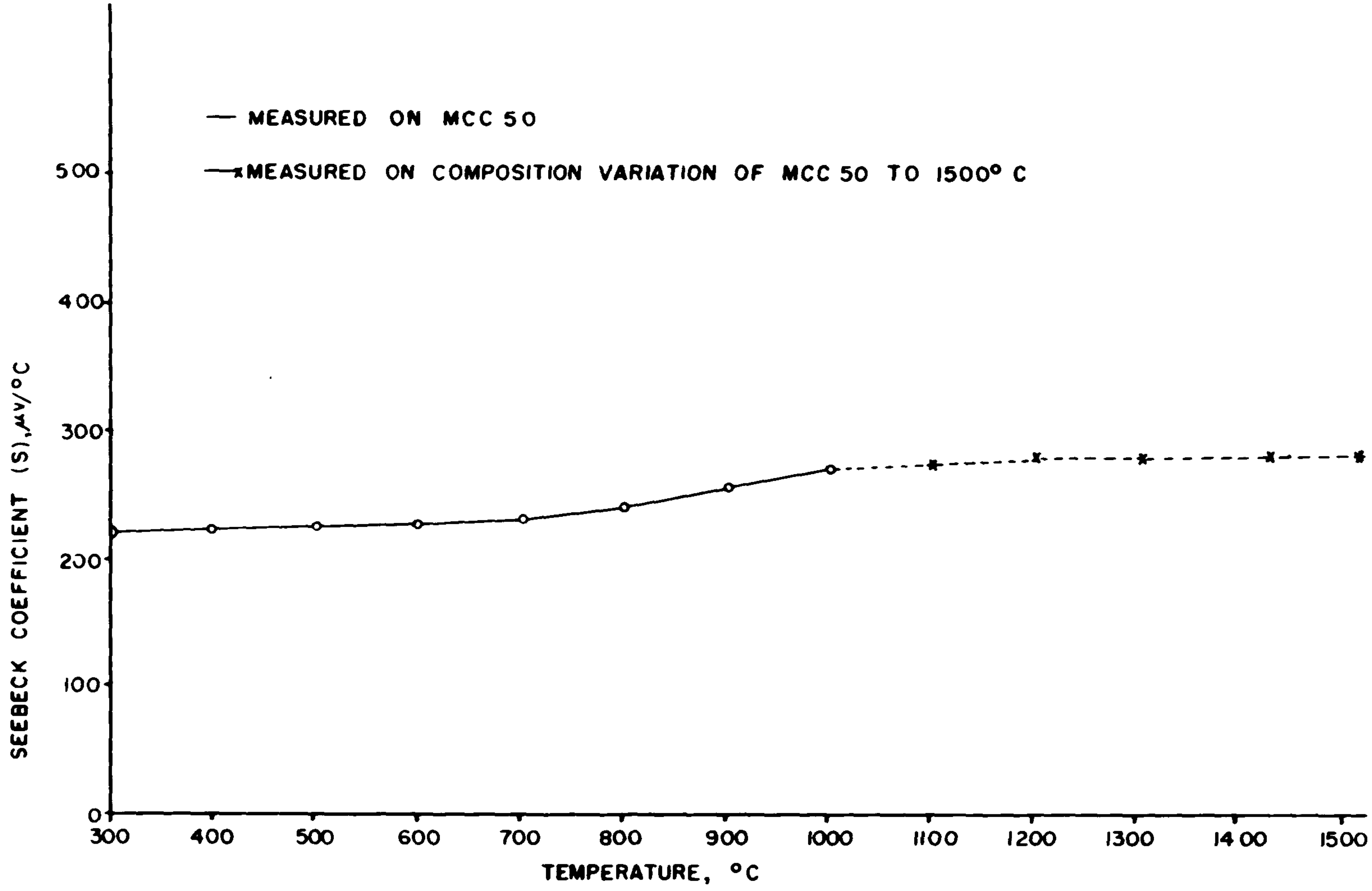

Figure 3. Seebeck Coefficient vs. Temperature for MCC 50 Thermoelectric Material (Revised April 1962)

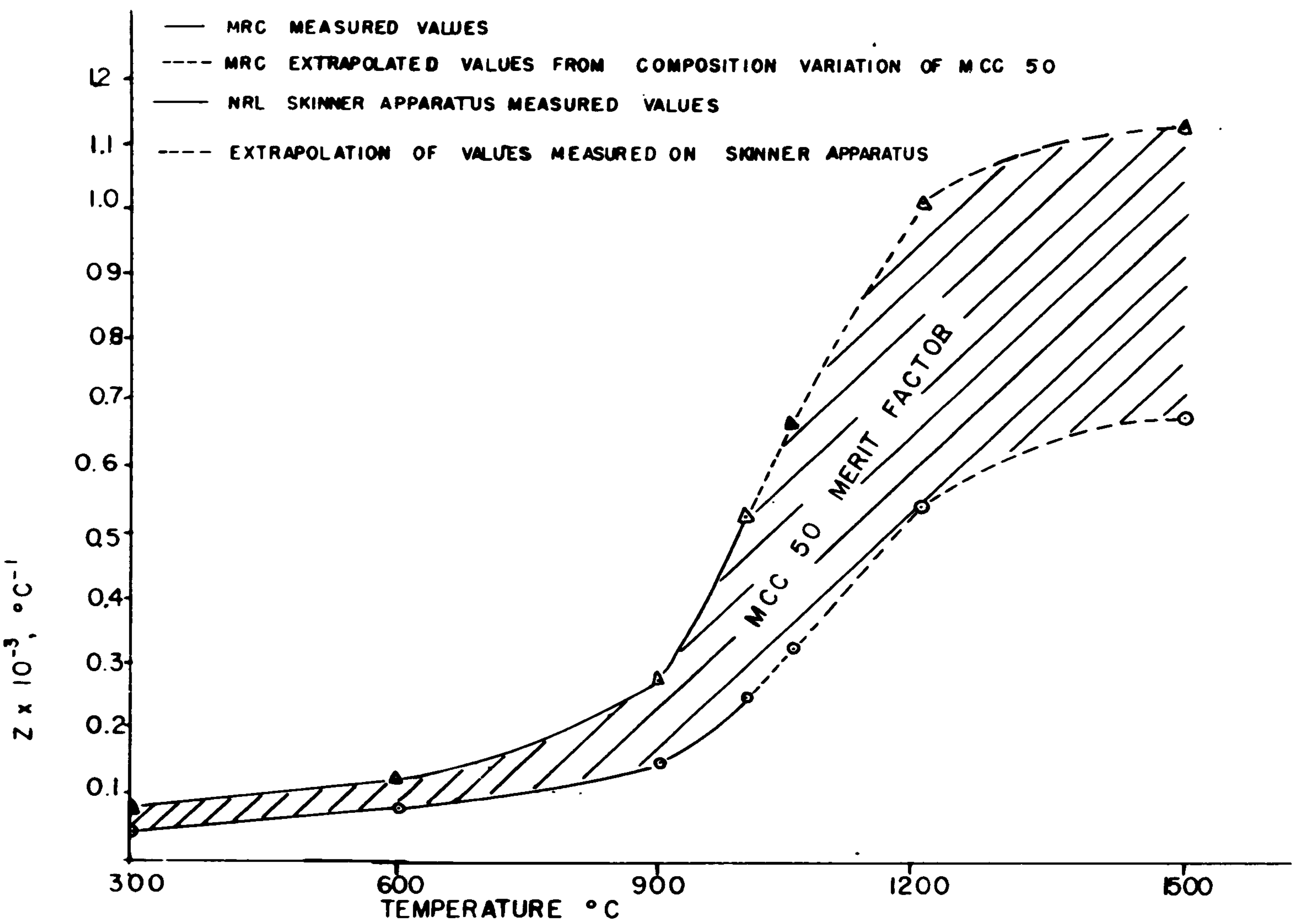

Figure 4. Merit Factors vs. Temperature for MCC 50 Thermoelectric Materials

PHASE I - JUNCTION MODULES

A. Selection of Material Several criteria were used in screening and selecting of junction materials for use in the end product generator. These included:

1. Relative resistance to thermal shock.

2. Relative resistance to solid-state diffusion damage with time and temperature at the interfaces between the MCC 50 and the candidate junction materials.

3. Relative sublimation losses.

4. Relative ease of fabrication in module form.

5. Effect on thermoelectric properties of modules.

As discussed below, resistance to thermal shock proved to be the most important criterion in narrowing the choice of junction materials. Results of sublimation, junction diffusion damage and other screening tests are discussed in succeeding sections.

Fourteen commercially available, refractory and highly conductive materials were originally surveyed as candidate junction materials. Five of these were eliminated during the first quarter of the project. Evaluation of the following materials continued during this quarter.

tantalum	chromium	tungsten
columbium	carbon	molybdenum
zirconium	titanium	hafnium

Nickel-free stainless steel (type 446) was studied as an intermediary material for the brazing or diffusion bonding of several of the above materials.

Thin low-strength junctions were produced from 446 stainless steel, zirconium, chromium, titanium and hafnium with MCC 50, but it was impractical to form junctions of about 1/2" thickness, as desired for use in the 5-watt generator. Figure 5 shows a typical example of one of the attempts to produce a zirconium-MCC 50-zirconium module with 1/2" dia. x 1/2" long zirconium caps. To make this module, the MCC 50 material was first hot-pressed at about 2000°C. The resulting 1/2" dia. x 1/2" long MCC 50 cylinder was then attached to the zirconium caps at a temperature of about 1750°C. During cooling, however, the MCC 50 material (the black central portions in Figure 5) fractured from thermal shock. As may be noted from the MCC 50 material remaining on the top surfaces of the two zirconium caps, shown at the right and left of Figure 5, appreciable bonding between zirconium and MCC 50 occurred. The white material, shown on the zirconium cylinders, is boron nitride used as the die material during hot-pressing. Examination of the junction between zirconium and MCC 50

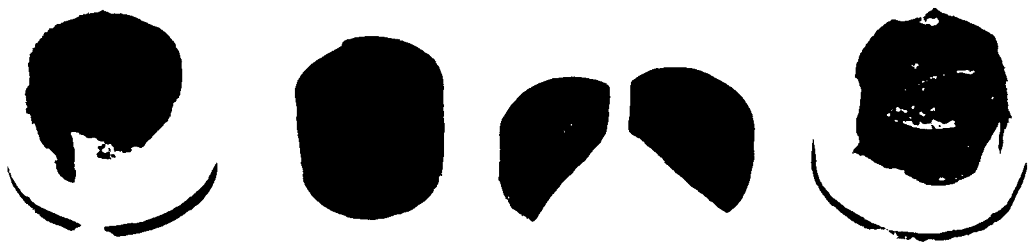

Figure 5. Result of Attempt to Bond Zirconium to MCC 50 by Hot-Pressing (Specimen HP7)

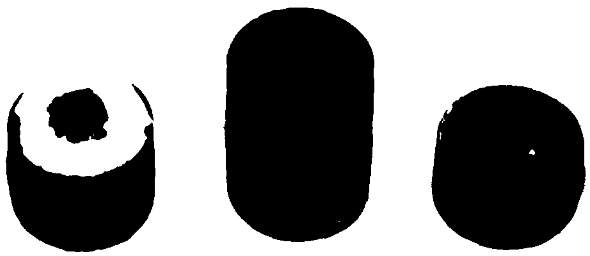

Figure 6. Result of Attempt to Bond Chromium to MCC 50 by Hot-Pressing (Specimen HP8)

indicated that the differences in the thermal coefficients of these materials was sufficient to prevent their being joined in thick cylinder form.

Figure 6 presents a typical result of attempts to join chromium to MCC 50. Bonding between the two materials was obtained at a hot-pressing temperature of 1500°C, but the junctions failed on cooling. The 1/2" diameter chromium caps used in this attempt are shown on each side of the central MCC 50 cylinder. The white material shown on the left chromium cap is boron nitride, the die material used.

Tantalum and columbium both formed junctions of promising strength and thickness. However, as with zirconium, considerable difficulty was encountered in maintaining the bond without fracture on cooling the module after hot-pressing, due to large differences in the thermal expansion coefficients. Figure 7 shows one tantalum-MCC 50-tantalum module that survived the cooling cycle after hot-pressing. This module was made by using a thin foil of zirconium as a braze intermediary material between the tantalum and MCC 50 materials and subjecting the module assembly to 2000°C at 5000 psi for several minutes. Unfortunately, this module failed to survive its first cycle when subjected to a thermal heating rate of only 50°C/minute.

Figure 8 shows a columbium-MCC 50-columbium module after it was fractured during evaluation by thermal cycling. This module was made by hot-pressing at 2000°C and 5000 psi, using zirconium as an intermediary or brazing material to promote bonding between the columbium and MCC 50. While this module also survived the initial cooling cycle after hot-pressing, it failed when subjected to an initial thermal cycle of only 50°C/minute during subsequent evaluation and was rejected from further immediate consideration for use in the end-product generator. Similar difficulties were experienced with titanium-MCC 50-titanium and hafnium-MCC 50-hafnium modules.

Carbon, tungsten and molybdenum are still under active consideration junction materials. A final selection is complicated by the conflicting advantages of each material. Carbon is the easier material to fabricate into module form with MCC 50. It is also the lightest and most readily machined junction material and is quite resistant to thermal shock. Tungsten and molybdenum are more difficult to fabricate into modules and less resistant to thermal shock, but their electrical characteristics and resistance to junction diffusion damage seem superior to those for carbon junctions. Final selection will be made on the basis of the best compromise of properties required for the specified generator.

B. Development of Joining Techniques to Make Modules Before modules could be screened for use in construction of the end product generator, the junction materials had to be joined to the thermoelectric material in a test module. To accomplish this, three techniques for joining were studied: 1) hot-pressing; 2) resistance welding; and 3) press-brazing.

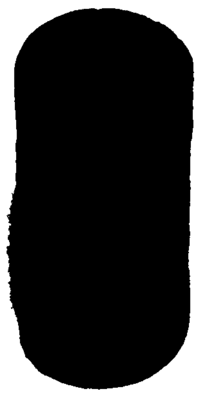

Figure 7. An MCC 50 Module With Tantalum Junctions as Assembled by Hot-Pressing (Specimen HP15)

Figure 8. Columbium-To-MCC 50 Bonded Areas as Exposed by Thermal Fracture (Specimen HP19) of Module

Simple hot-pressing assembly of modules has been moderately successful for all of the junction materials considered.

Hot-Press Joining Techniques Hot-pressing apparatus (Figure 9) consists of a graphite die assembly surrounded by a water-cooled induction coil. The die is lined with boron nitride, to preclude reaction with the thermoelectric or the junction materials. The thermoelectric material, in powder or presintered cylindrical form, is placed in the die and the junction material is also placed on each end of the thermoelectric material within the die assembly. The die assembly and its contents are heated by a high frequency power source through use of an induction coil. Temperatures well in excess of 2000°C can be attained. A pressure of 5000 psi is applied continuously by means of end rams of the die assembly, to promote intimate contact between the junction and thermoelectric materials. Chief disadvantage of this technique is the difficulty in accurately controlling temperature during the hot-pressing operation; however, this has been minimized satisfactorily through technique development.

Satisfactory carbon (graphite) junction modules of reproducible quality have been produced by the hot-press technique. Figure 10 shows one such typical carbon-MCC 50-carbon module. This module would require only machining to permit its use in the end-product generator, if the MCC 50 carbon module is selected for use in the final generator.

Difficulties have been encountered in reproducing modules using molybdenum and tungsten junction materials, due to the tendency of these elements to unpredictably form intermediate compounds with MCC 50 during joining operations. An approach to obtaining low resistance bonding between MCC 50 and molybdenum is illustrated in Figure 11, which shows a molybdenum module tightly attached to the center face of an MCC 50 cylinder. On the basis of the promise shown by the partial surface bonding obtained with specimens like that of Figure 11, experimental hot-pressings were conducted until large area bonding of molybdenum and tungsten to MCC 50 was achieved on a reproducible basis.

Several test modules were fabricated from step or profiled type molybdenum and tungsten caps like those shown at the top and bottom of the sketch in Figure 12. The use of step-type interfaces theoretically should provide more permanent bonds by minimizing the directional continuity of the thermal stresses between the metal caps and the MCC 50 at their interfaces. However, tests to compare flat-interface metal-MCC 50 modules (Figure 1) to the step-type interface module (Figure 12) showed that for tungsten or molybdenum capped modules the flat-interface type design has better thermal stress resistance.

As discussed subsequently under the "Solid-State Diffusion Damage", section, tungsten and molybdenum appear more resistant to junction diffusion damage than carbon. However, carbon has better resistance to thermal shock than tungsten and molybdenum. Since neither carbon nor these metals have the desired combination of high resistance to

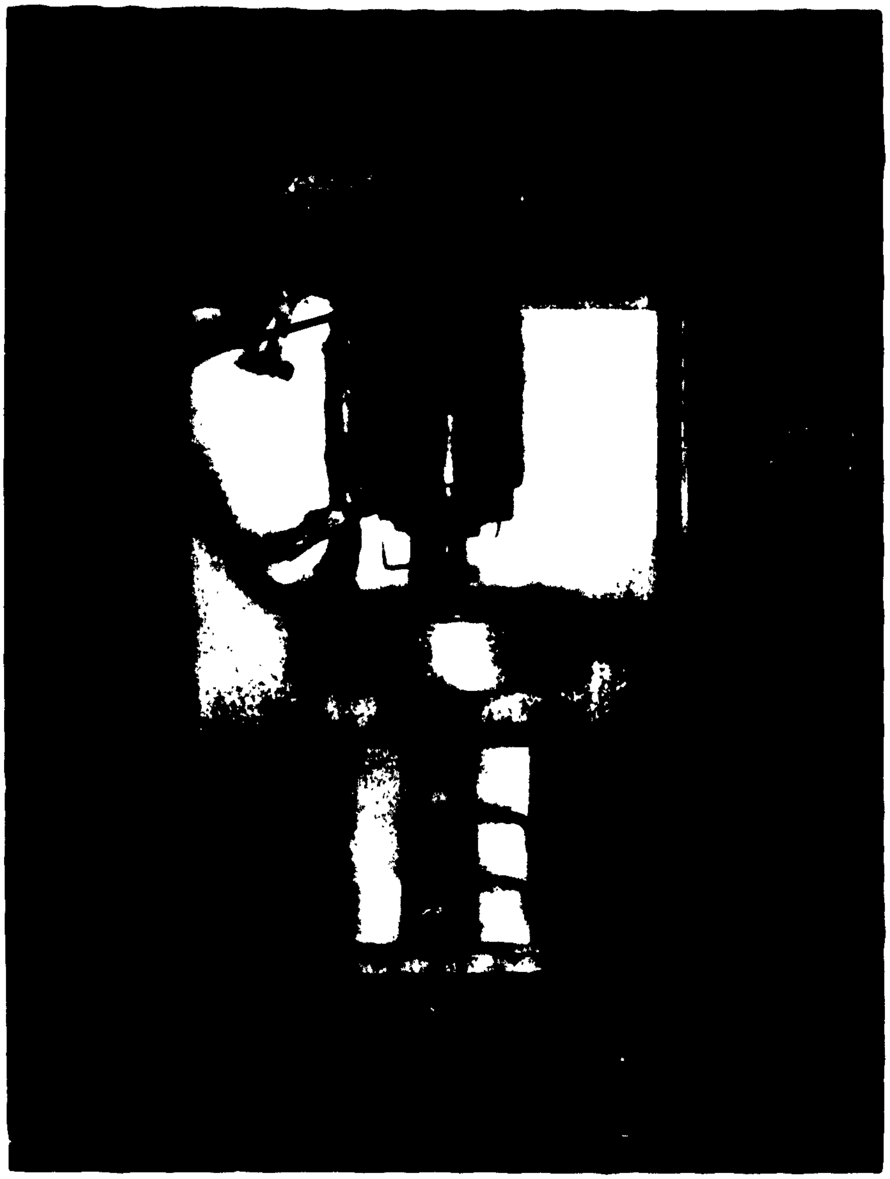

Figure 9. Hot-Press Equipment Used to Form Candidate Junction Modules With MCC 50

Figure 10. Typical Carbon-MCC 50-Carbon Module as Produced by Hot-Pressing (Specimen HP24)

Figure 11. View of an MCC 50-Molybdenum Interface Produced by Hot-Pressing. Note Small Nodule of Molybdenum Tightly Bonded to the Center of the Cylinder of MCC 50 (Specimen DMH3)

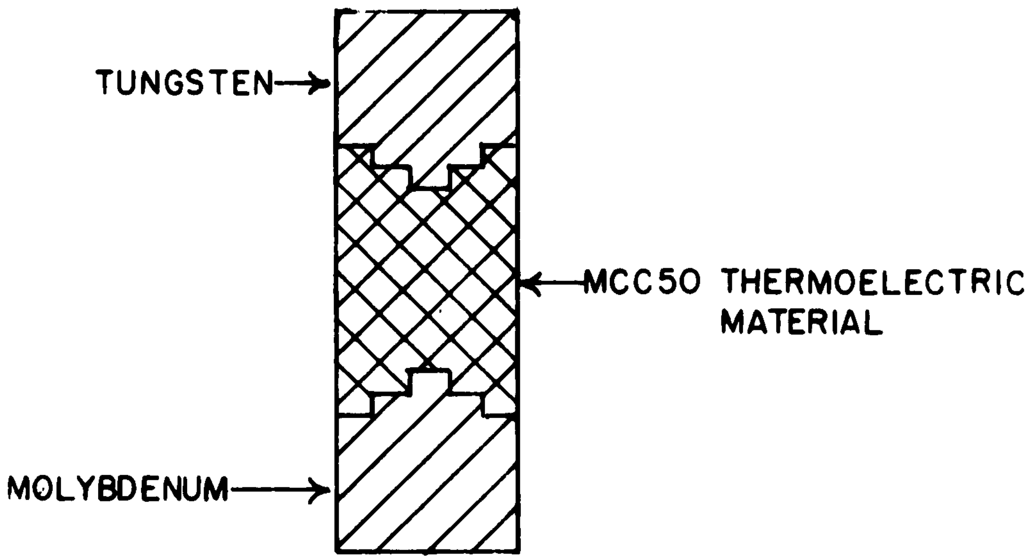

Figure 12. Step Profile Type Module Used to Produce Tungsten and Molybdenum Capped Modules

both diffusion-damage and thermal stress, the possibility of using carbon and molybdenum or tungsten to produce thermocouple modules was worth exploring. It was decided to produce a module using molybdenum for one junction with carbon as the other for MCC 50. Molybdenum was chosen because of its better machinability.

Figure 13 shows a hot-pressed module in which carbon was used for the top junction and a molybdenum cap was employed for the bottom junction with MCC 50. The carbon-MCC 50 interface was of the flat type while molybdenum-MCC 50 junction was step-type. The use of a carbon junction permits ready machining for adaptation to special hot or cold attachments. The slot and small hole shown in the bottom (molybdenum) cap permit insertion of a thermocouple and electrical leads for measuring temperatures and electrical properties of the module during thermal shock tests. Figure 14 shows the module of Figure 13 as it looked after being thermally fractured on exposure to a heat rate of 50°C/minute. In this case, the bond between the molybdenum and MCC 50 was poor and the sharp corners of the steps in MCC 50 material apparently contributed to thermal failure.

Figure 15 shows a hot-pressed module of MCC 50 fitted with an upper cap of carbon and a lower cap of tungsten bonded to MCC 50 with a step profile interface. Like that in Figure 13, this module has been prepared for thermal shock testing.

On the basis of experience obtained in producing substantial numbers of satisfactory test modules of MCC 50 joined with carbon, tungsten or molybdenum, the following finalized hot-pressing conditions will produce useful carbon-MCC 50-carbon modules for incorporation into the end product generator.

Condition	Range
Hot-press temperature	2000-2200°C
Pressure during peak temperature	4000-5000 psi
Time required at temperature and pressure	4-10 minutes
Die Material	boron nitride

Some work remains to be done in finalizing the hot-press conditions for use in producing molybdenum and tungsten capped modules.

Resistance Welding Joining Technique   High-current resistance-welding apparatus (Figure 16) employs dies to maintain alignment of the junction and thermoelectric materials during joining. For the dies, nonconducting materials, such as alumina, boron nitride, thoria, stabilized zirconia, and others, may be used. The thermoelectric material is inserted in the center of the die and the junction material is introduced at each end. Male rams, as used for hot-pressing, apply pressure to a vertical assembly of the junction and thermoelectric materials. A relative low pressure (100-200 psi) is usually adequate when the major portion of the heat is developed at the interface of the materials to be joined.

Figure 13. Hot-Pressed Module With a Step-Type Interface Lower Junction of Molybdenum and Flat Interface Upper Junction of Carbon (Specimen HP33)

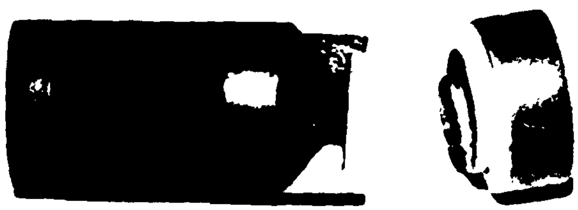

Figure 14. View of the Molybdenum-MCC 50 Bonded Area of the Module in Figure 13, as Exposed by Thermal Fracture (Specimen HP33)

Figure 15. Hot-Pressed Carbon-MCC 50-Tungsten Module in Which the Lower (Tungsten) Cap is Joined to MCC 50 With a Step-Type Interface Surface (Specimen HP34)

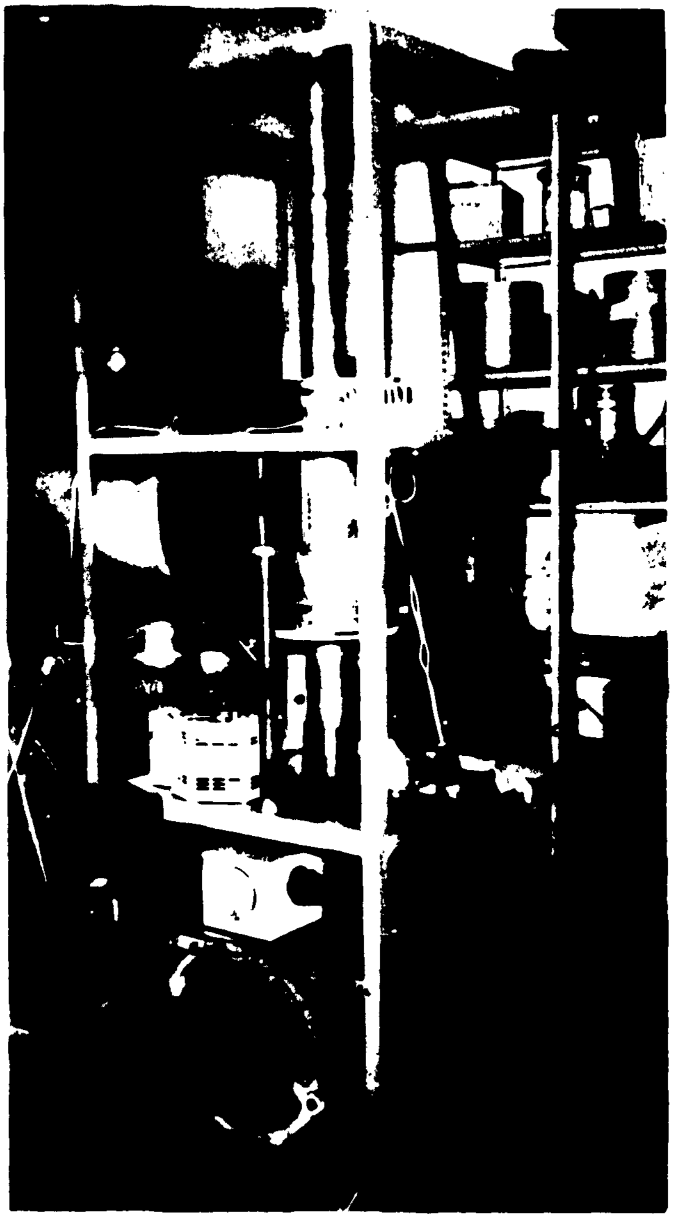

Figure 16. Apparatus Used to Form Candidate Modules by High-Current Welding Technique

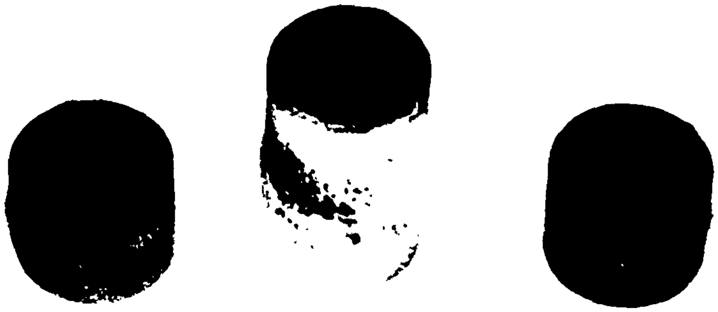

Figure 17. Mechanically Fractured Tungsten-MCC 50-Tungsten Module Made by Resistance Welding Technique. (Specimen RR4)

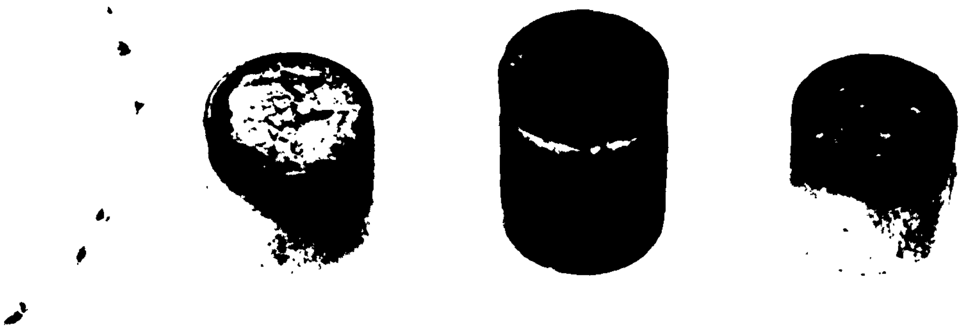

Figure 18. Resistance Welded Molybdenum-MCC 50-Molybdenum Module After Mechanical Fracture to Show Degree of Bonding (Specimen RR5)

A special resistance-heating furnace first heats the assembly to about 1000°C. To start the welding process, 200-300 amps A.C. at 10-15 volts are passed in series through the junction module assembly. The flow of such large currents through the thermoelectric junction materials in series generates heat both within the materials and at their interfaces. As with the hot-pressing technique, accurate control of joining temperature is difficult.

Several partially successful modules were produced by this method. Mechanically fractured specimens of some typical modules, shown in Figures 17 and 18, show that a rather satisfactory broad area bond can be obtained between MCC 50 and tungsten or molybdenum. The assemblies pictured were produced in alumina dies, protected by a hydrogen atmosphere, and preheated to 1000°C under an applied stress of 143 psi. Upon reaching 1000°C, the die assembly was heated to 2000°C in 5 minutes by applying a steadily increasing current from zero to 300 amps at 10 volts, A. C. The assembly was held at 2000°C for about 30 seconds, after which the current was steadily decreased to zero with a 5-minute period. Power to the furnace was turned off and the entire die and furnace assembly was cooled to room temperature within a 3-4 hour period. High quality hot-pressed cylinders of MCC 50 must be provided for use with this joining technique.

Although sound, mechanically strong bonds of MCC 50 with both tungsten and molybdenum can be achieved with the resistance welding method, temperature and pressure are troublesome to control. In addition, a separate hot-pressing operation to produce high quality MCC 50 cylinders is required. With the hot-pressing method both the MCC 50 and junction cap materials can be simultaneously produced via powder metallurgical techniques. In view of the good results obtained in forming modules via hot-pressing and by press-brazing (described below), no further work on the resistance welding technique is planned.

<u>Press-Braze Joining Technique</u> The press-braze technique, referred to in the first quarterly as "the brazing or diffusion-bonding technique" for joining , might be considered a modification of the hot-pressing and resistance-welding techniques. As with these methods, induction or resistance heat sources provide heat needed for bonding. Pressure up to 5000 psi is applied at the interfaces of the materials to be joined. Unlike the other two methods, an intermediate or brazing material is introduced between the thermoelectric and the junction material. For example, tungsten, which is not readily bonded directly to MCC 50 regardless of temperature and pressure, will bond to this material when a thin sheet of 446 stainless steel is used as a brazing material between the tungsten and MCC 50, and the joint is heated above the melting point of the stainless steel. Under these conditions, 446 alloy diffuses into both the junction and the thermoelectric material, bonding together two otherwise non-bondable materials. A schematic showing the arrangement of the thermoelectric, brazing and junction materials as they are placed in a boron nitride-lined graphite die is shown in Figure 19.

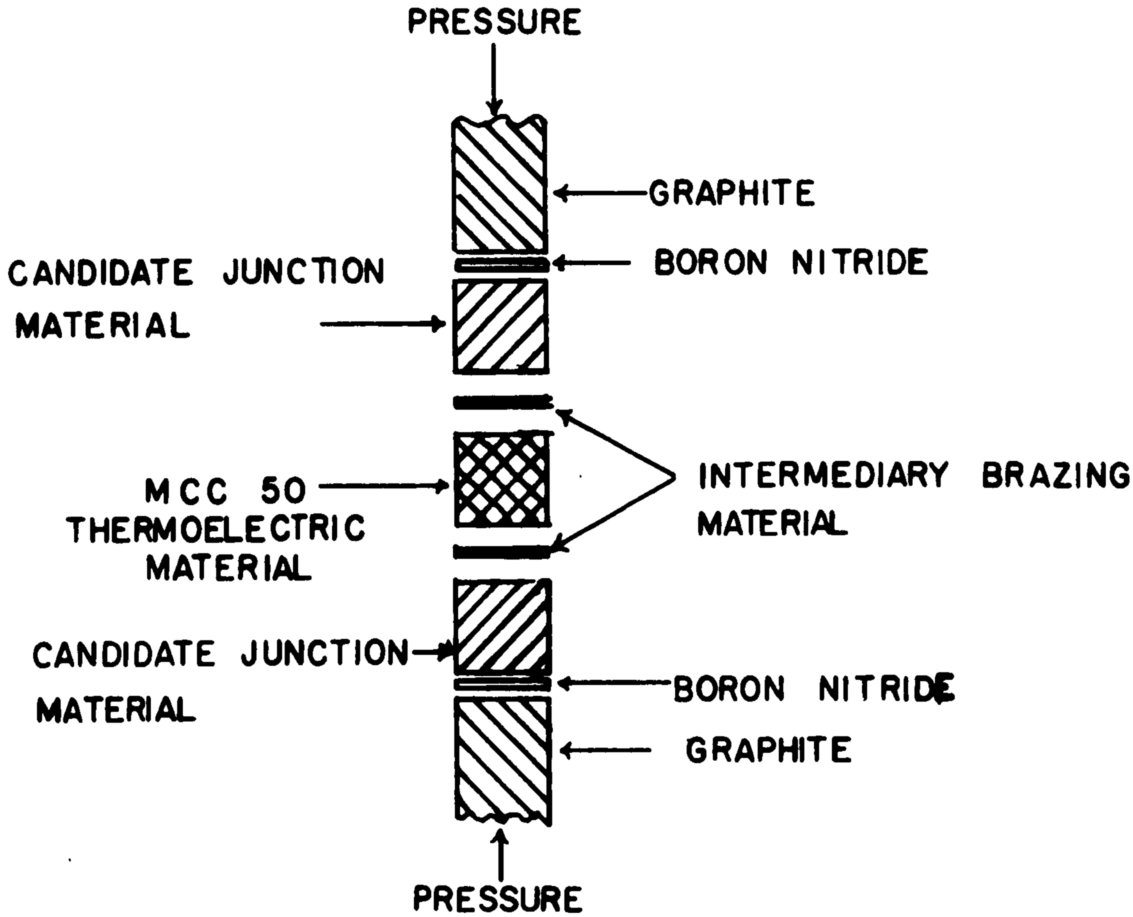

Figure 19. Schematic Arrangement of Materials to be Placed in a Graphite Die for Joining by the Hot-Press/ Braze Method.

The induction heated hot-press unit shown in Figure 9 is used to heat module components under pressure. This technique, titled the hot-press/braze joining method, has produced useful modules of MCC 50 with tungsten and molybdenum caps. Elemental zirconium has been found to be superior to 446 stainless steel as the brazing material. Typical high quality modules of MCC 50 capped with molybdenum and tungsten are shown in Figures 20 and 21.

If for the final generator molybdenum or tungsten junction caps are used in conjunction with MCC 50, the hot-press/braze joining method will be used to produce the modules.

PHASE II - TESTING OF MATERIALS AND MODULES

A. Sublimation Tests Prior to this contract, MCC 50 had not been tested under high temperature, high vacuum conditions. Data on rate of weight loss sustained by the thermoelectric material under a vacuum of 10^{-5} mm Hg at 1200°C, or higher, is required in order to predict sublimation losses for the 5-watt generator under space conditions. Accordingly, an apparatus (Figure 22) was fabricated to measure sublimation loss of MCC 50 between 1200°C and 1500°C at 10^{-5} mm Hg. The apparatus consists of a high temperature resistance-type furnace positioned around an impervious refractory tube. It was built by modifying available equipment.

The test specimen is placed within the refractory tube in the hot zone of the furnace. The sublimation rate is determined by measuring the weight loss per unit of time.

Sublimation testing was started on sample 59-1-I of MCC 50 material, 1/2" dia. x 3/8" long, at 1200°C in a vacuum of 1-5 x 10^{-6} mm Hg. The test was interrupted after 50, 150 and 250 hours exposure, to determine weight losses. Table 1 below shows the weight loss vs time at temperature.

TABLE 1. SUBLIMATION TEST ON MCC 50 at 1200°C and 1-5x10^{-6} mm Hg
Sample 59-1-I, Density 99.9%+ of Theoretical

Exposure, hr.	Weight, g.	Cumulative Wt. Loss, %	Loss per Hour,* %
0	2.8563	-	-
50	2.8524	0.137	2.69×10^{-3}
150	2.8502	0.214	0.77×10^{-3}
250	2.8482	0.284	0.70×10^{-3}

Note: *% Loss per hour based on each preceding time interval.

Figure 20. Molybdenum-MCC 50-Molybdenum Module Made by Hot-Press/Braze Method Using Zirconium as the Brazing Material. Module Made by the Hot-Press/ Braze Technique (Specimen HP9A)

Figure 21. Tungsten-MCC 50-Tungsten Module Formed by Hot-Press/Braze Method Using Zirconium as the Brazing Material (Specimen HP23)

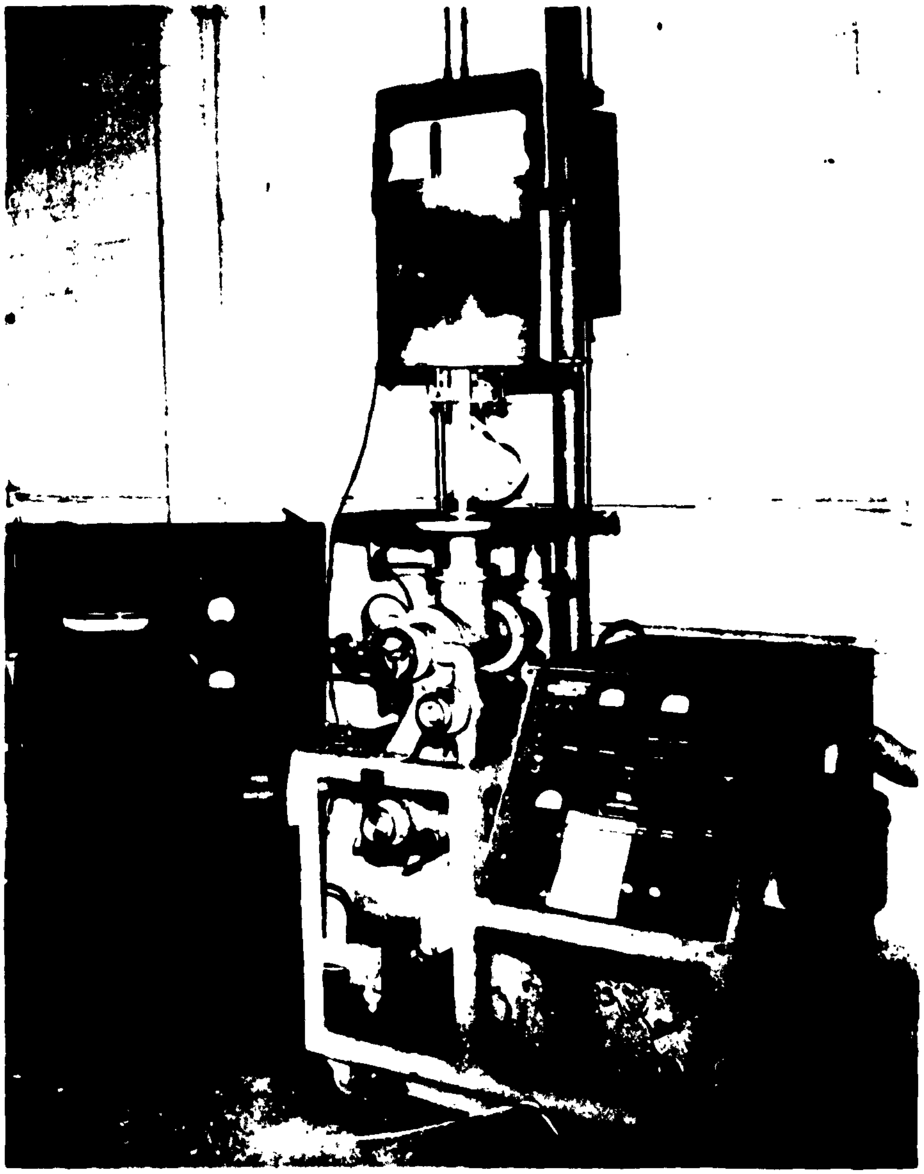

Figure 22. Apparatus for Sublimation Rate Testing of Thermoelectric Materials and Junction Module at 1200°C and 10^{-5} mm Hg.

The relatively high sublimation loss during the first 50 hours is believed due to volatile material from previous handling and processing. Extrapolation of a plot of weight loss vs time (Figure 23) indicates that nearly 0.1% weight loss may be due to this volatile material.

Furnace control failure after an accumulated 300 hours exposure caused the temperature to rise above 1400°C and resulted in the loss of the test and the sample.

After the apparatus was repaired, 500 hours exposure at 1200°C and 2-3 x 10^{-6} mm Hg vacuum were accumulated on a second MCC 50 sample. The test data are recorded n Table 2.

TABLE 2. SUBLIMATION TEST ON MCC 50 at 1200°C and 2-3x10^{-6} mm Hg
Sample 60-D, Density 97.1% of Theoretical

Exposure, hr.	Weight, g.	Cumulative Wt. Loss, %	Loss per Hour, %
0	4.1801	-	-
50	4.1678	0.294	5.90x10^{-3}
150	4.1633	0.402	1.08x10^{-3}
220	4.1615	0.445	0.62x10^{-3}
320	4.1599	0.483	0.38x10^{-3}
420	4.1587	0.512	0.29x10^{-3}
500	4.1580	0.529	0.21x10^{-3}

A plot of the cumulative weight loss vs time for this sample (Figure 24) illustrates again the high initial loss rate, attributed to volatile material present from processing and handling. The higher initial loss for this sample was attributed to its slightly lower density. By extrapolation, the data in Figure 24 indicates that the total weight lost by sublimation at 1200°C in a vacuum of 10^{-5} to 10^{-6} mm Hg should be less than 0.75% after 1000 hours exposure.

Sublimation testing of MCC 50 sample 60B at 1300°C has started. A total of 151 hours under vacuum of 4-9 x 10^{-6} mm Hg has been accumulated. After 60 and 151 hours exposure, cumulative losses were 0.98% and 1.62% respectively.

Tungsten-MCC 50-tungsten module, exposed to 1200°C for 100 hours in a vacuum of 1 x 10^{-5} mm Hg, sustained a negligible weight loss. However, mechanical failure of one of the tungsten-MCC 50 junctions occurred during subsequent handling of the specimen. A molybdenum-bonded module, prepared by an improved pressing technique, also exhibited negligible weight loss. Carbon-bonded modules, while retaining their mechanical strength, generally exhibit minor weight losses under greater than 10^{-5} mm Hg and 1200 C. On the basis of the sublimation rate loss tests, it is estimated that a generator operating at 1200°C in a vacuum of 10^{-5} mm Hg would lose less than 1% of its power generating capacity in 1000 hours, the ultimate design goal for the end product generator.

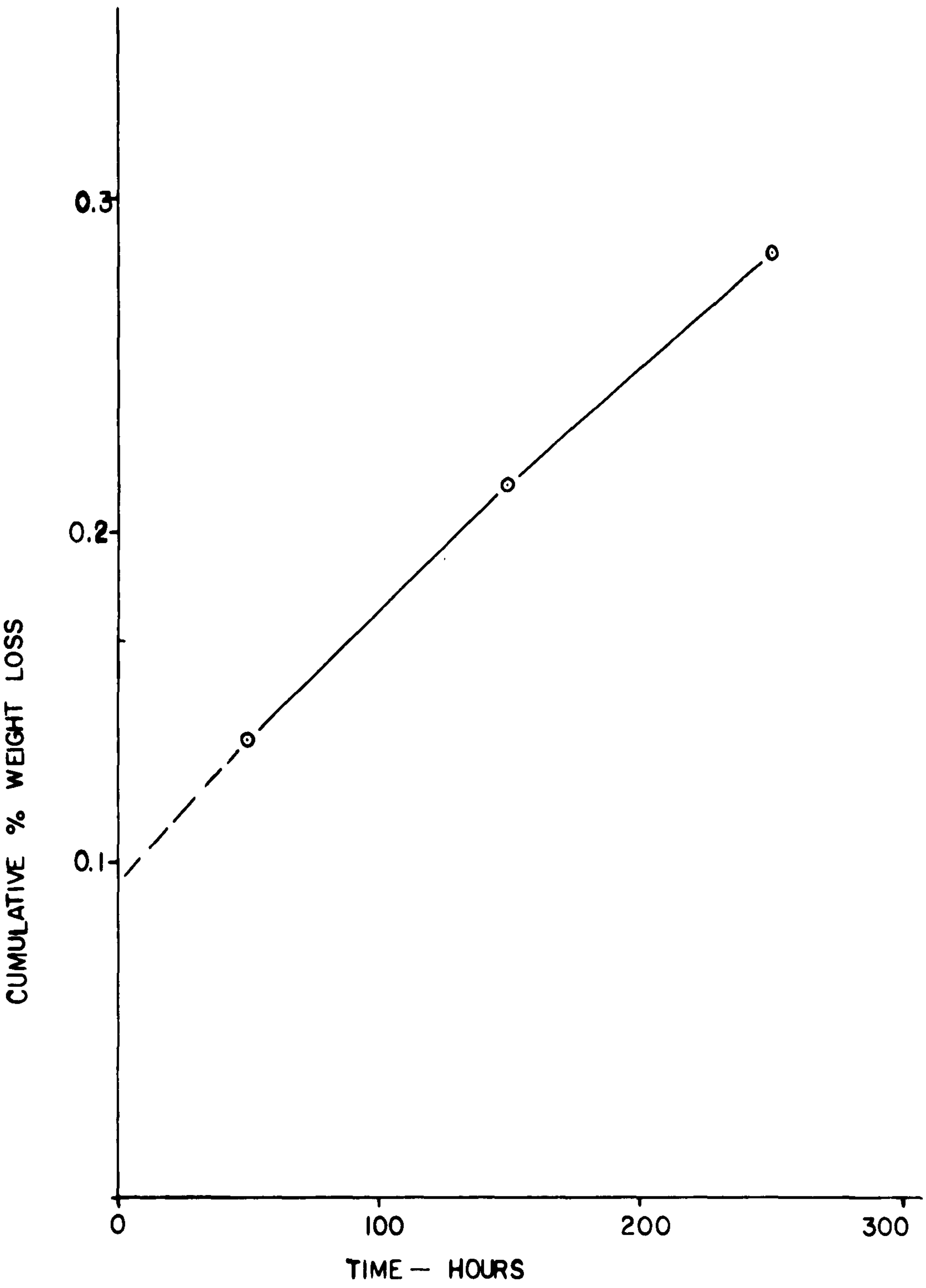

Figure 25. Sublimation Losses of MCC 50 Sample 59-1-I

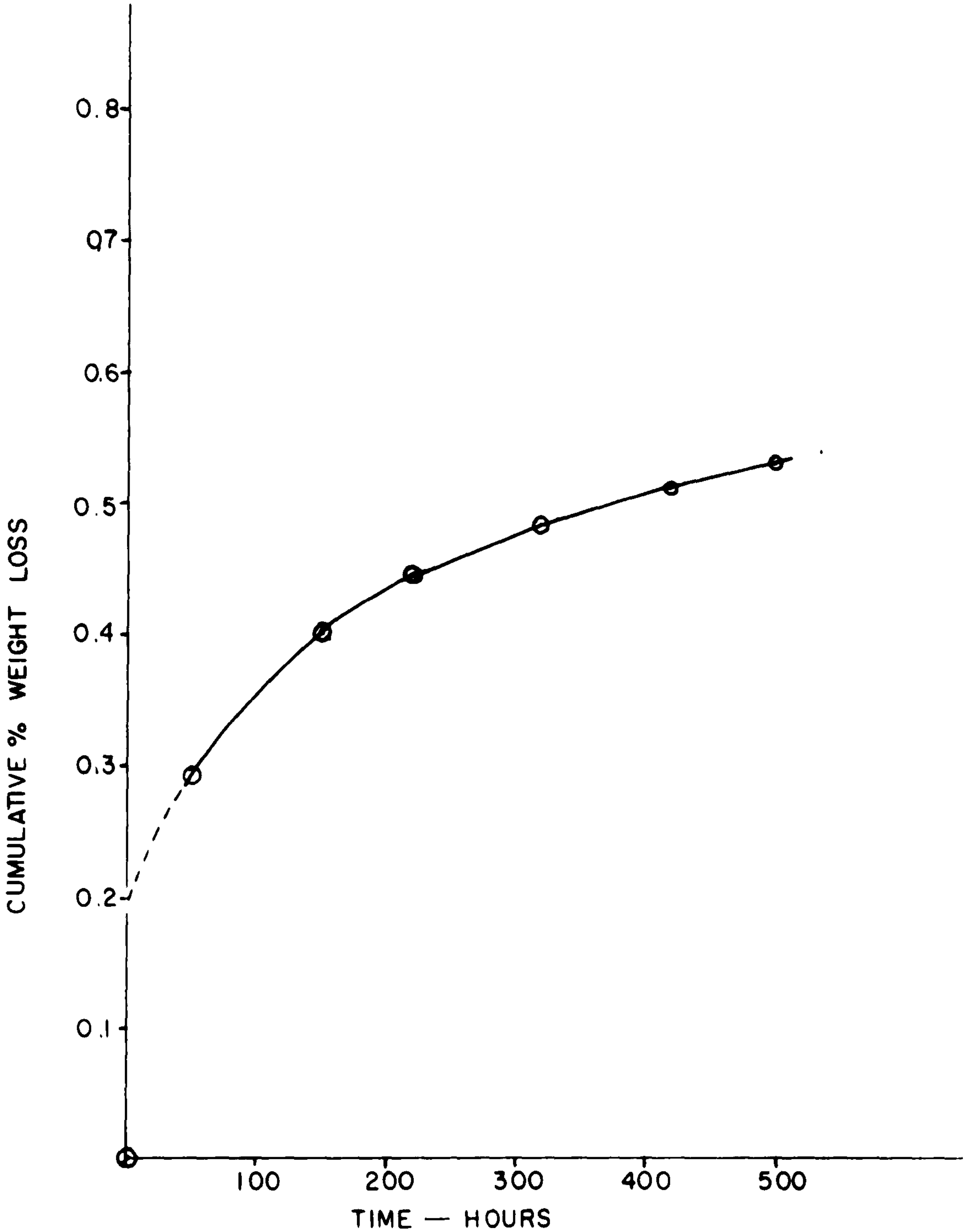

Figure 24. Sublimation Losses of MCC 50 Sample 60D

B. Thermal Cycling Tests on Modules Apparatus was completed for screening candidate modules for thermal shock resistance and to evaluate a new thermal cycling test heater unit. This apparatus, shown in Figure 25, permits a wide variation of thermal heating and cooling cycles and is capable of test temperatures to 1500°C. It provides for close simulation of the thermal cycling conditions apt to be encountered by a generator receiving energy from a solar type heat source while in orbit. For test purposes, heat is applied at the hot junction end of the module and energy is removed from the cold junction.

Carbon-MCC 50-carbon modules have been subjected to heating rates as high as 240°C per minute without mechanical failure. Cooling rates at the hot junction end of these modules have reached 500°C per minute during the first minute of cooling from 1340°C. After the first minute, this cooling rate cannot be maintained, owing to the reduced radiant heat transfer rate at lower temperatures.

A molybdenum capped module, HP-22, withstood hot junction heating rate of 200°C per minute, but the MCC 50 portion failed approximately midway between junctions when subjected to 225°C per minute heating rates. Figure 26 shows the module after failure. The location of the failure and the high heating rate necessary to cause failure indicates the potential capability of molybdenum as a junction material. Efforts to reproduce this module will be made.

Thus far it has been impossible to fabricate a tungsten-capped module that will withstand heating rates above 100°C per minute. However, the best module tested fractured partially at the interface and partially in the MCC 50 element, suggesting that sound junctions may be possible.

The best tantalum and columbium capped modules would not withstand heating rates as low as 40-60°C per minute. Failure occurred at the junction. Their performance was considered inadequate for the final generator.

Since thermal shock failures at the interface are largely due to use of materials differing too widely in coefficients of thermal expansion, it can be assumed that MCC 50 has a thermal expansion coefficient near those of carbon, tungsten and molybdenum. Columbium and tantalum have appreciably larger coefficients of expansion and are no longer considered potential junction materials. While it might be possible to develop an intermediate material to alleviate mismatch, this is not considered promising enough to be worth further effort at this time.

C. Measurement of Electrical Properties of Candidate Modules Seebeck coefficient (S) and electrical resistivity (ρ), as functions of temperature, were determined for selected modules consisting of MCC 50 with junction materials of carbon, molybdenum, tungsten and tantalum. Thermocouples used during these measurements were located in the junction

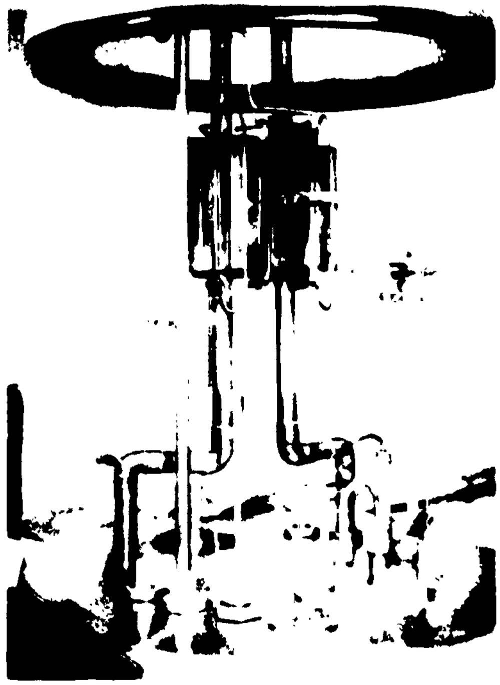

Figure 25. Completed Apparatus for Screening Candidate Modules for Thermal Shock Resistance.

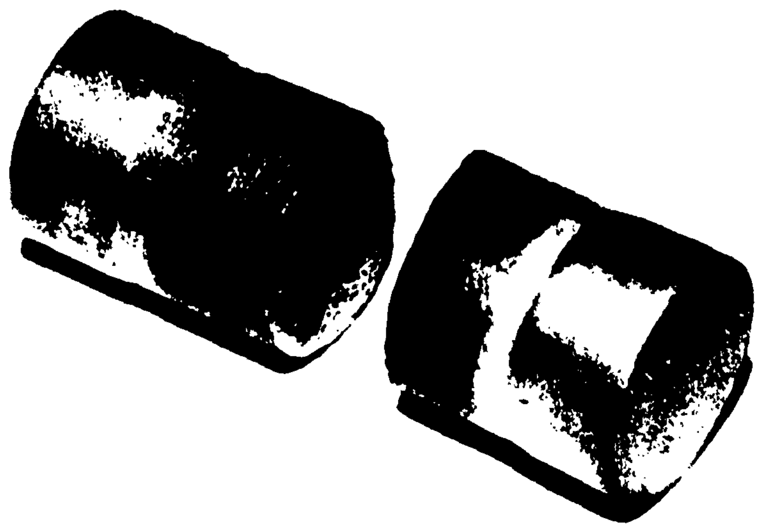

Figure 26. Molybdenum-MCC 50-Molybdenum Module After Being Subjected to Thermal Cycle Rate of 225°C Per Minute (Specimen HP22)

materials, so as to observe the over-all S and ρ , modules containing carbon, molybdenum and tungsten were subjected to 1200°C for 100 hours in vacuum. Upon completion of these tests, which are described in a later section, electrical properties were again determined. Dimensions of several types of modules subjected to such testing are presented in Table 3. Their electrical properties as functions of temperature, before and after exposure to 1200°C, are detailed in Tables 4 and 5. Essentially, there was little difference in the S^2/ρ vs temperature characteristics of the carbon-MCC 50-tungsten and molybdenum - MCC 50-molybdenum modules tested. S^2/ρ values above 3×10^{-6} watt per cm °K or higher are considered adequate for end product generator use.

Additional candidate modules were investigated to determine S and ρ as functions of temperature, for supplementary screening purposes. Modules in this group included carbon-MCC 50-tungsten, molybdenum-MCC 50-molybdenum and tantalum-MCC 50-tantalum. Owing to rather consistent thermal shock or mechanical failure of tantalum-MCC 50 junctions prior to measurements, electrical properties determined (Table 6) for such specimens were considered unreliable. Electrical properties of a specimen (M55-G),containing molybdenum end caps, is in reasonable agreement with data obtained earlier for a similar module (M59-1-T) prepared by an improved technique, and possessed slightly higher characteristic ratios of S^2/ρ than carbon bonded specimens. Over-all S^2/ρ data for carbon-MCC 50-tungsten module (M59-2-1) closely resembled that obtained for a typical carbon-MCC 50-carbon module (sample M59-1-L).

Data obtained for these three specimens indicate that over-all S and ρ values obtained for modules are in sufficient agreement with corresponding values for natural MCC 50 to qualify any of these junction materials for use in a thermoelectric generator. The mechanical and other properties of such modules should meet end product generator design requirements.

TABLE 3. DIMENSIONS OF TYPICAL MODULES SUBJECTED TO ELECTRICAL PROPERTY MEASUREMENTS

Sample	Junction Materials	Sample Length, in.	Diameter, in. Top Cap	MCC-50	Bottom Cap
C-59-2-L	Graphite (hot), tungsten (cold)	1.040	0.501	0.520	0.502
M-55-G	Molybdenum	1.200	0.534	0.506	0.527
M-59-2-A	Tantalum	1.102	0.532	0.527	0.532

TABLE 4. SEEBECK COEFFICIENT (S) AND RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR CARBON-MCC 50-TUNGSTEN MODULE

Specimen: C-59-2-L; carbon used as hot junction

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$, watts/cm°C
509.8	29.3	0.01059	196	3.61
605.7	29.6	0.00870	197	4.45
699.5	29.35	0.008038	198	4.87
787.9	29.8	0.008004	201	5.04
883.1	28.2	0.008091	217	5.84
785.8	29.3	0.008096	211	5.49
702.6	29.35	0.009396	208	4.59
522.3	29.45	0.01183	202	3.44

TABLE 5. SEEBECK COEFFICIENT (S) AND RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR MOLYBDENUM-MCC 50-MOLYBDENUM MODULE

Specimen: M55-G

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$ watts/cm°C
509.2	28.5	0.005566	160	4.62
601.1	28.0	0.00654	168	4.29
689.9	27.1	0.00622	175	4.89
775.5	26.5	0.00631	183	5.29
880.1	25.5	0.00652	193	5.70
770.4	25.75	0.00723	193	5.14
685.9	26.7	0.007065	182	4.69
599.6	27.2	0.008576	175	3.55
505.9	27.65	0.009018	172	3.26

TABLE 6. SEEBECK COEFFICIENT (S) RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR TANTALUM-MCC 50-TANTALUM MODULE

Specimen: M59-2-A

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$ watts/cm °C
496.5	28.7	0.04487	214	1.02
590.7	27.9	0.03799	217	1.24
677.5	28.5	0.03107	214	1.47
765.9	28.0	0.02918	222	1.69
856.1	27.4	0.02780	228	1.87
681.5	28.5	0.03628	231	2.32
497.7	29.9	0.05322	230	0.99

Note: One tantalum cap not firmly bonded during measurements

C. Solid-State Diffusion Rate Tests Degradation of thermoelectric properties of modules, and thus of a thermoelectric generator, would result if solid-state diffusion between junction materials and MCC 50 were significant at elevated temperatures in vacuum. To investigate this aspect, the following test procedure was employed.

Original S and ρ values for selected specimens were measured and samples were then subjected to 1200°C for 100 hours in a vacuum of 10^{-5} mm Hg or better. Weight losses were determined, physical characteristics were observed, and final S and ρ data were measured. Typical physical properties of modules subjected to such testing are presented in Table 7; detailed electrical properties, determined before and after such tests, are presented in Tables 8-13.

A molybdenum-MCC 50-molybdenum module (M-59-2-P) displayed essentially no change in S^2/ρ ratio after such testing; a tungsten-MCC 50-tungsten module (M-59-1-V) showed only a minor change under the same conditions. Carbon-bonded modules retained their mechanical strength with only a slight decrease in S^2/ρ after extended exposure to test conditions. While carbon capped modules presently appear to possess the most satisfactory combination of properties for the proposed application, their performance is not yet consistent from module to module. Tungsten and molybdenum-capped modules seem to show somewhat less damage due to solid-state diffusion phenomena than carbon-capped modules.

Further testing will be required to more fully determine which type module would be best suited from the viewpoint of maximizing the operating life of the end product generator by minimizing solid-state diffusion damage.

TABLE 7. DIMENSIONS AND WEIGHT LOSS OF SPECIMEN MODULES SUBJECTED TO SOLID-STATE DIFFUSION RATE TESTS FOR 100 HOURS AT 1200°C IN VACUUM OF 10^{-5} mm Hg

Specimen	Junction Material	Sample Length, (Inches)	Original Wt., gm.	Wt. Loss	Physical Condition After Test
M-59-1-K	Graphite	1.701	11.2487	0.42%	No difference noted
M-59-1-L	Graphite	1.685	11.1057	0.23%	No difference noted
M-59-1-T	Molybdenum	1.229	25.6066	0.13%	Mechanical failure of one junction during handling. Variety of cracks observed. MCC 50 color more gray than normal
M-59-1-U	Tungsten	1.210	44.7987	0.03%	Mechanical failure of one junction during handling
M-59-2-P	Molybdenum	1.104	22.1508	0.05%	No difference noted
M-59-2-M	Graphite*	1.858	12.7021	0.10%	No difference noted

Note: *"Graph-i-tite G" brand graphite.

TABLE 8. SEEBECK COEFFICIENT (S) AND RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR GRAPHITE-MCC 50-GRAPHITE MODULE BEFORE AND AFTER EXPOSURE TO 1200°C FOR 100 HRS IN VACUUM

Specimen: M-59-1-K

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$ watts/cm °C
		Before Diffusion Rate Test		
529.3	22.0	0.0128	219	3.75
608.7	22.1	0.0130	229	3.85
719.0	21.9	0.0127	236	4.38
810.5	22.1	0.0123	245	4.88
719.3	22.3	0.0130	230	4.07
625.4	22.8	0.0140	222	3.52
528.4	22.7	0.0163	220	2.97
529.5	22.2	0.0180	225	2.81
625.7	22.0	0.0152	225	3.33
718.6	21.9	0.0144	228	3.61
803.8	21.9	0.0136	240	4.23
881.7	21.2	0.0132	260	5.13
748.3	21.7	0.0138	234	3.97
669.0	22.2	0.0153	226	3.34
		After 100 hrs at 1200°C in vacuum		
531.7	23.0	0.0213	226	2.40
621.9	22.9	0.0186	227	2.77
716.8	22.8	0.0186	229	3.12
800.2	21.4	0.0157	242	3.73
893.0	20.6	0.0143	242	4.10
758.0	22.1	0.0162	238	3.49
673.9	22.5	0.0176	237	3.19

TABLE 9. SEEBECK COEFFICIENT (S) AND RESISITIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR GRAPHITE-MCC 50-GRAPHITE MODULE BEFORE AND AFTER EXPOSURE TO 1200°C FOR 100 HRS IN VACUUM

Specimen: M-59-1-L

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$ watts/cm °C
	Before Diffusion Rate Test			
541.0	23.4	0.0131	230	4.04
635.8	23.45	0.0112	224	4.48
718.5	23.0	0.0104	225	4.87
808.0	22.35	0.0098	230	5.40
899.0	21.2	0.0094	238	6.03
760.2	22.65	0.0104	233	5.22
668.4	23.9	0.0112	228	4.64
	After 100 hrs at 1200°C in vacuum			
520.3	24.4	0.0206	236	2.71
606.3	23.7	0.0182	244	3.26
694.8	23.4	0.0166	246	3.65
799.4	22.9	0.0154	250	4.06
863.3	21.4	0.0144	261	4.74
887.1	21.0	0.0149	263	4.64
705.5	22.4	0.0164	255	3.96
609.3	22.2	0.0182	261	3.74
516.6	23.4	0.0209	248	2.94

TABLE 10. SEEBECK COEFFICIENT (S) AND RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR MOLYBDENUM-MCC 50-MOLYBDENUM MODULE BEFORE AND AFTER EXPOSURE TO 1200°C FOR 100 HRS IN VACUUM

Specimen: M-59-1-T

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$ watts/cm °C
		Before Diffusion Rate Test		
540.9	28.4	0.00782	194	4.81
630.9	28.0	0.00737	198	5.32
716.0	27.6	0.00704	205	5.97
802.2	29.1	0.00704	201	5.74
715.0	28.4	0.00757	206	5.61
630.7	26.7	0.00817	207	5.24
503.1	26.6	0.00940	199	4.21
		After 100 hrs at 1200°C in Vacuum*		
499.8	28.3	0.02645	197	1.47
589.5	28.2	0.02689	201	1.50
678.2	27.2	0.02823	210	1.56
819.5	26.5	0.02889	214	1.59

Note: *One molybdenum junction not firmly bonded during measurements.

TABLE 11. SEEBECK COEFFICIENT (S) AND RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR TUNGSTEN-MCC 50-TUNGSTEN MODULE BEFORE AND AFTER EXPOSURE TO 1200°C FOR 100 HRS IN VACUUM

Specimen: M-59-1-U

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	$S^2/\rho \times 10^6$ watts/cm °C
	Before Diffusion Rate Test			
525.8	26.7	0.00628	197	6.18
611.8	27.4	0.00577	194	6.53
689.6	26.4	0.00550	204	7.56
775.9	25.6	0.00530	218	8.97
692.5	27.2	0.00559	202	7.30
596.0	27.7	0.00597	195	6.37
501.6	26.7	0.00665	197	5.83
	After 100 hrs at 1200°C in Vacuum			
517.8	29.7	0.00941	201	4.72
608.5	30.3	0.00830	204	5.00
700.3	30.0	0.00763	205	5.31
788.9	30.0	0.00735	205	5.72
696.6	30.4	0.00761	204	5.44
608.3	30.7	0.00795	202	5.11

TABLE 12. SEEBECK COEFFICIENT (S) AND RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR MOLYBDENUM-MCC 50-MOLYBDENUM MODULE BEFORE AND AFTER EXPOSURE TO 1200°C FOR 100 HRS IN VACUUM

Specimen: M-59-2-P

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	S^2/ρ x10^6 watts/cm°C
	Before Diffusion Rate Test			
622.7	36.9	0.006398	197	6.07
717.2	35.7	0.006002	201	6.71
806.1	35.1	0.005970	201	6.74
874.8	32.65	0.006139	220	7.83
792.3	33.9	0.006488	219	7.40
707.0	35.0	0.006817	207	6.30
615.5	35.55	0.007249	208	5.97
	After 100 hrs at 1200°C in Vacuum			
624.2	28.8	0.008753	225	5.75
739.6	29.5	0.008174	226	6.22
829.4	29.1	0.007828	233	6.96
893.1	28.0	0.007582	243	7.77
805.7	29.3	0.007948	234	6.88
723.1	30.1	0.008354	225	6.15
621.9	29.5	0.008966	225	5.63

TABLE 13. SEEBECK COEFFICIENT (S) RESISTIVITY (ρ) AS FUNCTIONS OF TEMPERATURE FOR GRAPHITE-MCC 50-GRAPHITE MODULE BEFORE AND AFTER EXPOSURE TO 1200°C FOR 100 HRS IN VACUUM

Specimen: M-59-2-M

Hot Junction, °C	Temperature Differential, °C	ρ, ohm-cm	S, μvolts/°C	S^2/ρ x10^6 watts/cm °C
		Before Diffusion Rate Test		
550.4	23.55	0.00686	207	6.24
637.9	23.55	0.00643	206	6.60
756.1	22.5	0.00594	212	7.58
876.4	20.0	0.00634	238	8.90
910.3	18.70	0.006476	254	9.98
873.0	18.33	0.006903	272	10.68
755.5	20.05	0.007407	258	8.99
637.4	21.7	0.007965	245	7.52
543.0	22.45	0.008805	239	6.49
		After 100 hrs at 1200°C in Vacuum		
551.6	28.20	0.0149	224	3.38
650.8	24.62	0.01356	222	3.63
750.4	24.30	0.01271	217	3.72
831.7	24.40	0.0122	209	3.58
926.8	22.53	0.0115	202	3.50

PHASE III - FABRICATION AND TESTING OF THE 5-WATT GENERATOR

A small four-element generator was constructed from carbon-MCC 50-carbon modules to evaluate fabrication techniques for the 5-watt generator. This unit and a spare module are shown in Figure 27. The hardware and measuring equipment required to test this unit under simulated operating conditions is being assembled. Testing should be underway in April.

On the basis of results to date, a parallel-connected generator consisting of a number of modules fastened between hot and cold junction plats, illustrated in Figure 28, appears feasible.

III. CONCLUSIONS

It was possible to narrow the selection of candidate junction materials to carbon, tungsten and molybdenum. A hot-press/braze technique for joining these junction materials to produce useful MCC 50 modules was developed. Sublimation rate loss tests conducted for 500 hours at 1200°C in a vacuum of $2\text{-}4 \times 10^{-6}$ mm Hg showed a 0.53% weight loss. This indicates less than a 1% loss in power generation capabilities from this cause in 1000 hours operation.

Measurements of the electrical properties of modules before and after exposure for 100 hours at 1200°C in a vacuum of 10^{-5} to 10^{-6} mm Hg indicate that solid-state diffusion damage at junction interfaces should not cause power failure of the end product device on a 1000-hour mission. Carbon-capped modules are better than molybdenum and tungsten-capped ones with respect to resistance to thermal stresses apt to be encountered in space orbits. Molybdenum and tungsten-capped modules exhibit better resistance to solid-state diffusion damage than carbon-capped ones. Further attempts should be made to increase the resistance of carbon to diffusion damage as well as improving the resistance of molybdenum and tungsten to thermal shock resistance before final selection of junction materials for use in the fabrication of the end product generator.

IV. FUTURE PLANS

During the next quarter efforts will be made to fabricate both the end product generator and the facilities required to test it. Some further testing to determine the optimum type of module will be carried on and further sublimation rate loss measurements to 1300°C at 10^{-5} to 10^{-6} mm Hg will be made. Testing of the end product generator should be started.

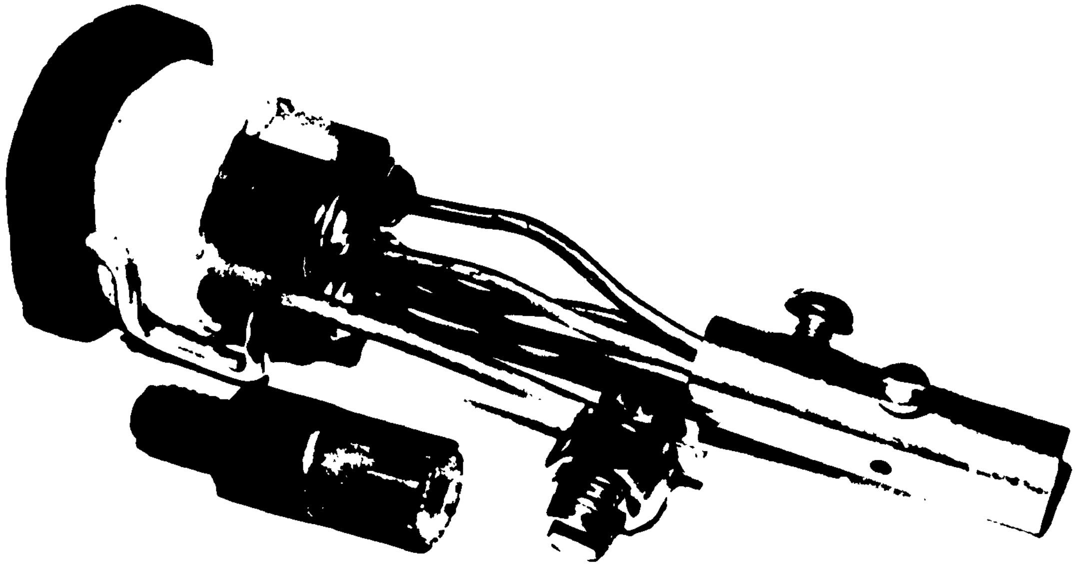

Figure 27. Prototype Generator With Four Carbon-MCC 50-Carbon Type Modules for Evaluation of Fabrication Techniques

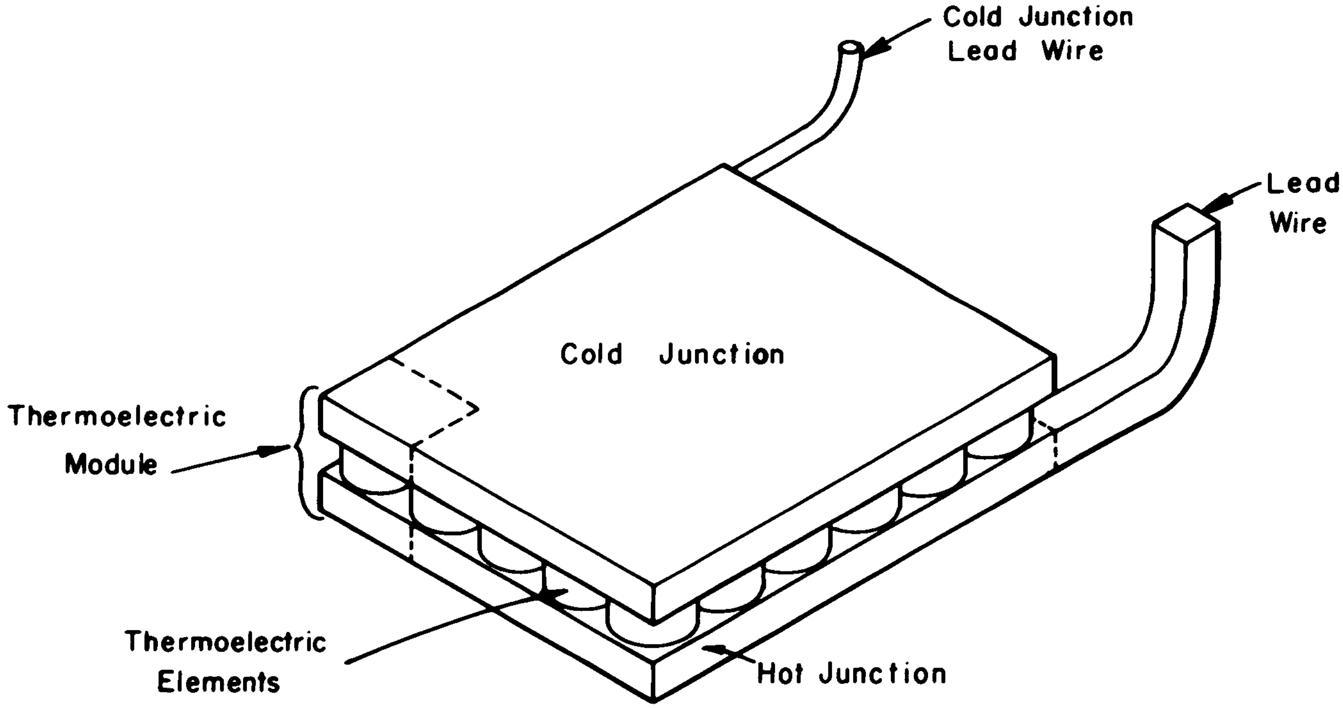

Figure 28. Conceptual Design of 5-Watt Generator